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A Bond Length – Bond Valence Relationship for Carbon – Nitrogen Bonds

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Running Title: A Bond Length – Bond Valence Relationship for C-N Bonds

Abstract

In a recent study, Pauling's relationship between bond length and valence was derived along with a definition for his fitting parameter *b* that incorporates the orbital exponents for each atom contributing to the bond of interest. The values of *b* for various bonds, including C-N bonds, were calculated using the orbital exponent data. In this study, Pauling's correlation between bond length and bond valence, as well as his valence sum rule, were used with the recently-derived definition for *b* in order to produce a relationship specifically applicable to C-N bonds. The resulting equation was checked against published x-ray diffraction data for 430 C-N bonds. It is expected, and shown by the data presented in this study, that these equations relating the bond length and bond valence of C-N bonds have sufficient applicability and accuracy for use in any bonding environment, regardless of physical state or oxidation number.

Introduction

The length and valence (strength) of a chemical bond influences the reactivity and structure of the molecule. Consequently, a systematic method of determining bond valence has always been of interest to chemists. In 1929, Linus Pauling (Pauling 1929) published his five rules of chemical bonding which could be used for predicting crystal structures. Pauling's second rule proposes the idea of local charge neutrality, commonly known as the valence sum rule, whereby the charge of an anion is neutralized by the sum of the adjacent cationic charges, while any cationic charge is neutralized by adjacent anionic charges. In terms of bond valence, the total valence at any one atom is equal to the sum of that atom's individual bond valences. In 1947 (Pauling 1947), Pauling published the following bond length-valence relationship:

$$s = \exp\left(\frac{R_o - R}{b}\right) \quad (1)$$

where *s* is the bond valence, which corresponds to the number of pairs of electrons contributing to the bond, R_o is the length of a chemical bond with unit valence, *R* is an observed bond length, and *b* is an empirical fitting parameter. A wide range of determined values for the *b* parameter, anywhere from 0.25 to 0.65 Å (Hardcastle and Laffoon 2012), led to many inconsistencies in valence values, an issue that hindered the ability of chemists to compare findings. As a result, it was later proposed that a consistent value for *b* should be established as the average of this range, equaling 0.37 Å as a universal constant for *b*. This produced a consistent relationship with only one fitting parameter, R_o; however, when applied to shorter and longer bonds, the calculated valence was shown to be less reliable.

Theory

In 2013, Hardcastle derived Pauling's bond length-valence, including a new definition for the *b* fitting parameter. Since then, a slight modification has been made, resulting in the following equation:

$$b = \frac{2a_o}{(\xi_1 + \xi_2)} \quad (2)$$

where *b* depends on the Bohr radius of a hydrogen atom, a_o (0.529 Å), and the sum of the atomic orbital exponents for each of the atoms contributing to the bond. This definition produces values for *b* that are specific to the type of bond being addressed, a more accurate alternative to the average value of 0.37 Å assumed for any type of bond. Combining these values with Eq. (1) produces bond length-valence relationships that vary with bond types, as well.

Methodology

Bond length values were collected for C-N bonds from published x-ray diffraction data totaling 430 C-N bonds. Limiting the data to systems composed of carbon and nitrogen, the total valence at a single carbon or nitrogen atom was calculated by totaling its individual bond valences (see Supplemental). Bond valences were calculated using Eq. (3). Each bond with a length of approximately 4.5 Å or less was included in the calculation. Figure 1 shows the calculated valence of each bond, using Eq. (3), formed by a carbon atom (C1) to carbon and nitrogen atoms in the crystal (Vo et al. 2014).

C1 Environment		Vo 2014	
	Bond Length (Å)	Valence	
C-C Bonds	4.58	5.8458E-05	
	4.243	0.000168955	
	4.58	5.8458E-05	
	4.243	0.000168955	
	3.942	0.000435976	
	1.447	1.127130315	
	3.693	0.000955057	
	4.294	0.000143886	
	3.693	0.000955057	
	4.068	0.000293175	
	4.294	0.000143886	
C-N Bonds	4.072	0.000112852	
	3.565	0.000646944	
	2.363	0.040624071	
	3.565	0.000646944	
	3.388	0.001190195	
	2.363	0.040624071	
	3.771	0.000318228	
	3.388	0.001190195	
	3.771	0.000318228	
	3.731	0.000365232	
	3.561	0.000655918	
	1.139	2.751738002	
	3.561	0.000655918	
	3.867	0.000228636	
	3.867	0.000228636	
	4.17	8.0524E-05	
	4.124	9.43476E-05	
	4.17	8.0524E-05	
	4.124	9.43476E-05	
		3.970405992	Total

Figure 1. The bonding environment for a single carbon atom (C1) showing the bond lengths, calculated bond valences, and the total atomic valence.

Results and Discussion

Data analysis and error minimization relative to the expected atomic valence values led to a specific relationship for C-N bonds:

$$s_{C-N} = \exp\left[\frac{(1.425 - R)}{0.2984}\right] \quad (3)$$

This equation was shown to produce accurate valence values from published bond length data.

In a previous study by Hardcastle and Harris (Harris and Hardcastle 2015), bond relationships were derived and tested for C-C and C-O bonds. However, the approach to calculating total atomic valence for the carbon and oxygen atoms was recently found to be inadequate and a new method was implemented in the present study. Prior to this research, only the shortest few bond lengths were incorporated into the atomic valence calculation, ignoring any intermolecular bonds. The longer bonds between molecules correspond to valence values that can significantly affect the atomic valence of the target carbon or nitrogen, as shown in this study.

The total atom valence for a nitrogen-centered environment was found to be either 3.00 or 4.00 valence units. That is, nitrogen is capable of forming three bonds, or it can use its lone pair of electrons to form a fourth bond. Comparing the calculated atomic valences to the predicted valences, the total error for the C-N bonding was minimized by manipulating R_o, the length of a C-N bond having a bond number or bond order of exactly one. Due to the relative confidence in the orbital exponents, those values were not changed in order to minimize error, but were instead held constant.

The atomic orbital exponent for carbon was found to be $\xi_C = 1.6844$ from a very recent study (Hardcastle 2016) and that for nitrogen was found to be 1.8620 respectively, close to published values (Herman 2004). Substituting these values into Equation (2), results in a *b* parameter of 0.2984 Å for C-N bonds. Note that this value is much lower than the previously assumed universal constant of 0.37 Å set by Brown and Altermatt (Brown and Altermatt 1985). This leaves R_o in Eq. (1) as the only remaining fitting parameter which was found to be $R_o = 1.4250$ Å as the C-N bond length representing unit valence; that is, the ideal C-N single bond.

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Conclusion

The bond length – bond valence relationship proposed by Linus Pauling provides a useful tool for the prediction and evaluation of crystal structures when used in tandem with his valence sum rule. Until recently, his equation contained two fitting parameters, *b* and R_o, causing inconsistencies as various *b* values were determined. In the present study, we determined a reliable relationship for finding C-N bond valence from bond length based on using Eq (1) and using Eq. (2) to find the b parameter from atomic orbital exponents, and Ro from the best fit 430 C-N bond lengths. R_o for an ideal C-N bond of unit bond valence (bond order of 1) was found to be R_o = 1.4250 Å.

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